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Estimating degree of degradation of spilled oils based on relative abundance of aromatic compounds observed by paper spray ionization mass spectrometry

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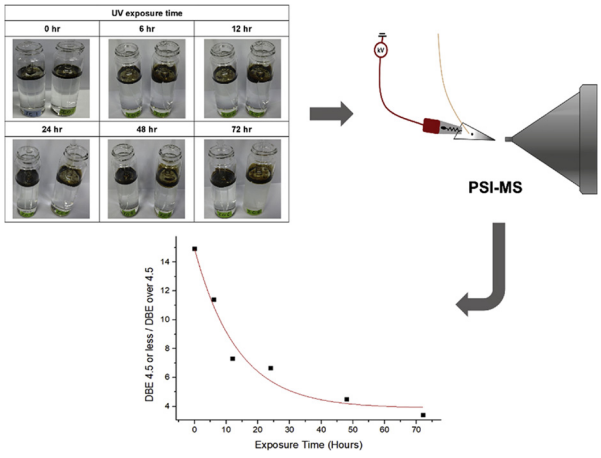
GRAPHICAL ABSTRACT



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ABSTRACT

Paper spray ionization mass spectrometry (PSI-MS) was applied for the first time to study temporal change of photo-oxidized and weathered oils subjected to degradation. PSI is chosen in this study because it is an optimal ionization technique for the analysis of degraded oils with limited sample quantity and prone to salt and particulate contamination. With PSI-MS, quantitative analysis of oils can be successfully performed with as little as 2 μg of oil sample. In addition, oil solutions containing up to 0.05% sodium chloride were successfully analyzed with PSI-MS. In the PSI-MS spectra of photo-degraded oils, the relative abundance of compounds having double equivalence value (DBE) ≥ 5 increased but those with DBE < 5 decreased in number. The summed abundance ratio of compounds having DBE < 5 and DBE ≥ 5 showed a negative exponential correlation with the duration of UV exposure in laboratory experiments. The same trend was observed from spilled oils obtained from the

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environment. Therefore, this ratio serves as an effective means to estimate the degree of weathering in spilled oils.

1. Introductions

Despite the development of various alternative energy sources, petroleum still remains major resource of the global primary energy consumption [1]. Increasing global demand for oil has caused extensive oil exploration, production, and transportation activities in recent years. Unexpected oil spills can, therefore, inevitably happen during the transportation of petroleum products. It is well known that the impact of an oil spill can be long-lasting [2–6] and cause severe damage to the environment, marine organisms, and human beings, as seen in previous large oil spill accidents such as the *Exxon Valdez* oil spill (EVOS), the *Hebei Spirit* oil spill (HSOS) [7] and the *Deepwater Horizon* oil spill (DWHOS) [8–13]. Once oil is spilled at sea, it spreads on the sea water by the wind, tides and currents. At the same time, the oil goes through various weathering processes such as evaporation, emulsification, biodegradation, photodegradation, and sedimentation [14–18]. These weathering processes cause significant changes in the physicochemical properties of the spilled oil [19–25]. In particular, ultraviolet (UV) radiation from the sun can significantly increase the toxicity of chemicals in spilled oil [26–31]. Studies on the characterization of spilled oil, therefore, are useful for estimating the behavior and fate of spilled oil, and can be helpful to establish diagnostic values of the source identification [32,33].

Mass spectrometry (MS) is one of the most important analytical techniques in complex mixture analysis, providing information on the chemical composition and structures (e.g., double bond equivalents, DBEs) based on accurate molecular weight. It can also provide further structural information through the molecular fragmentation patterns using MS/MS experiments. For successful MS analysis, it is necessary to select the proper ionization technique depending on the sample properties and instrument performance such as resolving power, accuracy and sensitivity. Electrospray ionization (ESI), atmospheric pressure photoionization (APPI), and atmospheric pressure chemical ionization (APCI) are the most commonly used ionization techniques in the field of petroleomics [34–38]. It is well known that ESI is good for the ionization of polar compounds [39–41] while APPI and APCI are useful for the ionization of non-polar or less polar analytes [39–44]. Even though these methods are useful, they are limited in certain cases. When direct infusion method is used, as it is typical for oil analysis, the constant infusion of sample is required. This can be problematic when the sample volume is limited, as is often the case for long-term oil spill studies. ESI is also sensitive to the presence of contaminants. Spilled oils recovered from the environment often include salts and particulates.

Paper spray ionization (PSI) and paper spray chemical ionization (PSCI) are fast and convenient ionization techniques for the direct analysis of various types of compounds [45–48]. PSI is mainly used to detect polar analytes (similar to ESI) and PSCI can be applied to study non-polar compounds (similar to APPI or APCI). Therefore, PSCI and PSI can be complimentary ionization methods suitable for analyzing environmental samples. Application of PSCI for the spilled oil analysis has been investigated and reported in the previous study [48]. However, the potential of PSI for analysis of oil and especially spilled oil has not been previously explored.

In this work, we identified the advantages of PSI-MS usage for environmental sample analysis and used PSI to characterize spilled oil samples. To the best of our knowledge, this is the first study using PSI-MS to investigate weathering effects of spilled oils at the molecular level.

2. Materials and methods

2.1. Sample preparation

Spilled oil samples from the *Hebei Spirit* oil spill (HSOS) were collected and provided by the Korea Institute of Ocean Science and Technology (KIOST). In this accident, approximately 10,900 tons of three different types of crude oil (Kuwait export crude, Iranian heavy crude, and UAE Upper Zakum crude) were released into the sea and spread by tides and the wind. Further details on the oil spill accident can be found in previous reports [33,49]. Different weathering stages of spilled oil samples were collected from the Gurumpo beach in South Korea at 7 and 19 days after the spill. As a control, three types of oils were mixed according to the spilled proportion. The location of the sampling site is provided in the supporting information (Figure S1).

For photo-oxidation experiments, 0.1 g of Iranian Heavy crude oil (IHC) was floated onto 10 mL of filtered sea water in a precleaned 20 mL vial. The oil sample was subjected to UV radiation and samples were collected after 6, 12, 24, 48, and 72 h of exposure. For the control sample, oil was prepared with the same manner except that it was thoroughly wrapped with aluminum foil to block the UV radiation. A metal halide lamp (Philips MSD 250/2 30 H) was used to obtain the different stages of weathered oil samples. The UV radiation was optimized to resemble the radiation from natural sun light [50]. The irradiance of UV-A, UV-B, and UV-C light from this lamp was 19.9, 1.91, and 0.21 W/m^2, respectively. The temperature in the UV chamber was maintained at 15–20 °C using a cooling system. A list of samples used in this study is given in Table S1.

2.2. Mass spectrometry and data processing

Our experimental setup for PSI-MS is the same as the one previously reported [48]. The instrument setup and an image of the PSI are provided in the supporting information (Figure S2). Approximately 50 μg of each oil sample was directly loaded onto the center of the paper tip using a glass Pasteur pipette (Volac, Poulten and Graf Ltd., U.K.). Hexane:2-butanol 50:50 (v/v) was used as spray solvent. For quantitative experiment, the spilled oil was dissolved in dichloromethane at 1000–9000 ppm and 1 μL of the sample was loaded onto the paper tip. After the paper was dried, 1 μL of 50 ppb sodium dodecyl sulfate (Sigma Aldrich, Japan) solution prepared in methanol was added directly on the sample spot as an internal standard. Sodium dodecyl sulfate was chosen in this study because it has good response in negative PSI-MS. To test salt tolerance of PSI, 2000 ppm spilled oil solutions in toluene and 0.1%, 0.01%, and 0% NaCl solutions in methanol were prepared. For ESI-MS, each concentration of NaCl solution was mixed with spilled oil solution at the 50:50 ratio (v/v). Then sample solution was infused by a syringe pump (Fusion 100 T, Chemyx, Stafford, TX, USA) at a flow rate of 10 μL/min. Samples were analyzed using a Q-Exactive mass spectrometer (Thermo Fisher Scientific Inc., Rockford, IL, USA) in negative ion mode over the range of m/z 180 − 1500, providing a mass resolution of 100,000 (FWHM) at m/z 400. The spray voltage and the S-lens radio frequency (RF) level were set at 3900 V and 50 V, respectively. The capillary temperature was set at 300 °C and the sheath gas flow rate was set to 7 (arbitrary units). For PSI-MS, 5 μL of spilled oil solution dissolved in toluene was loaded on the paper tip, then the same volume of each concentration of NaCl solution was loaded on the paper tip. The sample-loaded paper was placed in front of the orifice of the